NEW APPLICATIONS OF PERCHLORIC ACID, CERATE AND o-PHENANTHROLINES TO ANALYTICAL CHEMISTRY

BY

JAMES SHERWOOD FRITZ

B.S., James Millikin University, 1946
M.S., University of Illinois, 1946

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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PART I

A NEW METHOD FOR THE DETERMINATION OF BUTTERFAT IN ICE CREAM

Introduction

The Babcock determination of butterfat in milk, cream and certain other milk products has been an established procedure for over 50 years. The test is rapid, accurate to a satisfactory degree, requires a minimum of skill for its successful application and is very nominal in unit cost. The unmodified Babcock butterfat test cannot be applied successfully to dairy products containing added sugar due to the charring action of the sulfuric acid. This of course precludes the application of this test to ice cream. Preliminary experiments indicated that perchloric acid possesses desirable solvent properties somewhat similar to those exhibited by strong sulfuric acid on milk and cream, but does not char sugar appreciably. It was therefore the purpose of this investigation to show that perchloric acid could be used as the basis for modifying the standard Babcock test to make it applicable to ice cream mix for the determination of butterfat.

Experimental Procedure

Standard Babcock equipment was used throughout. A 9 gram portion of the ice cream to be analyzed was mixed with 10 - 30 ml. of the perchloric acid reagent used and the mixture digested in a boiling waterbath until the fat began to separate out as a separate layer. The test bottle and contents were then centrifuged, tempered at 60°C. for 5 minutes and the percent fat read. The Mojonnier test, a commercial adaptation of the official Röse-Gottlieb method (1) was employed to carry out control determinations. All samples tested were evaluated both by the Mojonnier method and the perchloric acid process simultaneously and the results

compared.

Conclusions

1. A mixture of 72% perchloric acid and glacial acetic acid (ratio 1 : 1 by volume) was found to be the most satisfactory reagent studied for the separation of butterfat in ice cream. If 30 ml. of this reagent is added, 5 minutes digestion and 2 minutes centrifugation are required. Dilution with the same reagent is employed to bring the fat up into the calibrated neck of the test bottle.

2. By a slight modification in procedure, this same reagent can be used to determine the butterfat content of chocolate ice cream and evaporated milk.

3. The results obtained from over 300 analyses indicate that the perchloric-acetic acid method gives results which are in close agreement with the official method. This accuracy along with the simplicity and speed of this method, make it compare very favorably with various other proposed rapid methods. (2, 3, 4).

PART II

MICRO VOLUMETRIC DETERMINATION OF IRON AND ARSENIC

Introduction

The micro-volumetric determination of oxalate and the indirect determination of calcium as applied to blood plasma has been described by Salomon, Gabrio and Smith (5). Their procedure involved the titration of very small amounts of oxalic acid in a 2 F perchloric acid solution with a dilute, standard solution of perchlorato-ceric acid. It is the purpose of the present work to show that the same degree of accuracy results from an extension of the process to include the micro-titration of iron and arsenic.

Experimental Procedure

The procedure duplicated that previously described by Salomon *et al* (5) for the micro determination of calcium. The 0.001 N. perchlorate-ceric acid used was standardized against sodium oxalate (Bureau of Stds. No. 40e). An arsenious acid solution of known strength was prepared from pure arsenious oxide (Bureau of Stds. No. 83a) and weighed portions were taken for titration with cerate. A ferric perchlorate solution was prepared from pure iron wire and weighed portions were passed through a micro Jones reductor and titrated with cerate.

Results And Conclusions

1. Potentiometric titrations of 0.001 N. iron, oxalate and arsenite with 0.001 N. perchlorate-cerate show a big "break" in potential at the equivalence point (0.95 to 1.5 volts).

2. Iron and arsenite can be titrated with 0.001 N. perchlorato-cerate using nitro-ferroin as the indicator. The average error in these determinations was $\pm 0.5\%$. This compared favorably with the accuracy obtained in the spectrophotometric determination of iron.

3. It is possible to apply this method to the micro determination of arsenic in organic arsenic compounds with a fair degree of accuracy. The organic matter must first be destroyed by digestion with perchloric acid and the resulting arsenate reduced with sulfite.

PART III

1,10-PHENANTHROLINE FERROUS PERCHLORATE AND 2,2′-DIPYRIDYL FERROUS PERCHLORATE AS COLORIMETRIC IRON STANDARDS

Introduction

Calibration curves for the colorimetric iron determination with 1,10-phenanthroline or 2,2′-dipyridyl are generally pre-

pared by first preparing a standard iron solution from pure iron wire and then taking suitable portions, reducing the iron with hydroxylamine hydrochloride, adjusting the pH to 7, addition of the complexing reagent and dilution to a given volume. The present work demonstrates that 1,10-phenanthroline ferrous perchlorate (I) and 2,2′-dipyridyl ferrous perchlorate (II) can be used as primary standards for the preparation of these curves. The use of these salts is advantageous in that they have a very high equivalent weight and that iron standards can be prepared very conviently by merely dissolving weighed portions of the salt in water and diluting to the required volume.

Experimental

I and II were prepared by adding a slight excess of perchloric acid to a solution of the commercially available 0.025 M. ferrous sulfate complex. The remaining percipitate was collected, washed three times with cold water and dried two days over anhydrous magnesium perchlorate.

The purity of the salts thus prepared was demonstrated by evaporation to dryness with perchloric acid to destroy the organic matter and then titrating the residual iron by a micro titration with perchlorato-ceric acid as described in the previous section. The results of this determination indicated that both of these salts were essentially pure and anhydrous.

Color standards prepared from I and II were evaluated spectrophotometrically by measuring the transmittancy at 512 mμ and 520 mμ respectively. The curves thus obtained were then compared and found to agree with those obtained when the iron standards were prepared by the conventional method (using pure iron wire as a source of iron). In order to obtain the best results, all glassware must be scrupulously clean and double distilled "conductivity" water employed. Addition of a small amount of uncomplexed 1,10-phenanthroline or 2,2′-dipyridyl to the standards causes no error and appears to improve their stability somewhat.

PART IV

DETERMINATION OF HYDROGEN BOND STRENGTHS IN CERTAIN 1,10-PHENANTHROLINES

Introduction

1,10-Phenanthroline as well as the 5-bromo and 5-methyl derivatives form mono hydrates which are definite chemical entities with sharp and reproduceble melting points. Infra red data indicate that the water molecule is held through two hydrogen bonds to the ring nitrogens. When 1,10-phenanthroline monohydrate is heated, it dissociates reversably and rapidly into 1,10-phenanthroline and water. The purpose of this investigation is to measure the dissociation pressure of certain 1,10-phenanthroline monohydrates and hence the equilibrium constants for reactions of the type:

$$C_{12}H_8N_2.H_2O\ (s) = C_{12}H_8N_2\ (s) + H_2O\ (g)$$

From these data, measurements of the strengths of the hydrogen bonds can be readily obtained.

Experimental

The essential features of the apparatus employed are:

1. A pyrex sickle gauge sealed into the tube containing the sample.

2. A mercury manometer, the pressure differential of which was observed by a suitably disposed cathetometer.

3. A thermostat consisting of a Dewar-like pyrex vessel, the temperature of which could be adjusted by the ebullition of a suitable organic liquid contained between the walls.

The sample employed was an intimate mixture of approximately equal weights of the hydrate and the anhydrous material. After the sample has been introduced, the apparatus is evacuated and the manometer read. As the sample tube is heated and vapor pressure is developed, the pressure differential is compensated by allowing air to leak into the external system. At equilibrium, the sickle gauge is brought

exactly to its null point and the manometer again read, the difference in readings being the dissociation pressure at the equilibrium temperature.

Results

The thermodynamic quantity, ΔH for the preceding reaction represents the amount of energy required to remove one mole of water from 1,10-phenanthroline and thus break two hydrogen bonds. It is therefore assumed that $\Delta H/2$ represents the strength of a single hydrogen bond. Accordingly, hydrogen bond strengths of 7.25, 6.50 and 6.60 K.cal/mole were found for the hydrates of 1,10-phenanthroline and the 5-bromo and 5-methyl derivatives respectively.

It has been predicted (6) that a deuterium bond should be somewhat stronger than the corresponding hydrogen bond. Accordingly, 1,10-phenanthroline mono deuterate was prepared and the dissociation pressure measured. The strength found for deuterium bond was 7.30 K.cal/mole which confirms this prediction.

PART V

3,5,6,8-TETRAMETHYL-1,10-PHENANTHROLINE AS A REAGENT FOR IDENTIFICATION AND MICRO DETERMINATION OF THE PERCHLORATE ION

Introduction

No completely satisfactory means has yet been developed for the detection and determination of perchlorate. Among the various reagents proposed for use in this connection are methylene blue (7), nitron, tetraphenylarsonium chloride and various alkaloids (8). Although 3,5,6,8-tetramethyl-1,10-phenanthroline (III) is not available in large quantities, it does seem promising for use in the identification and microdetermination of perchlorate.

Experimental

The reagent employed was a solution made by dissolving 100 mg. of III in 100 ml. of water and 0.5 ml. of HCl. Tests for qualitative sensitivity indicated that the limit of identification is about 0.01 mg. of perchlorate in a solution containing 100 p.p.m. of the perchlorate ion. The major interfering cations are Ag^{+}, Hg^{+}, Hg^{++}, Sn^{++}, Sn^{++++} and Cd^{++}. Many anion interferences are noted but interference from anions in the soluble group are notably absent. The perchlorate ion can thus be detected in the presence of ClO_3^-, NO_3^-, BrO_3^- and IO_3^-, a separation which is difficult to accomplish by other means.

Quantitative determinations of perchlorate on a micro scale were carried out by precipitation of the perchlorate with III in a filter-beaker of 9 ml. capacity. The precipitate was washed with two or three 0.5 ml. of ice cold, dilute (1 : 10) III and dried to a constant weight at 110°C. The precipitate has the theoretical composition of the mono perchlorate of III rather than the di-perchlorate salt as was originally expected. Results obtained indicate that this method is accurate to within 3% of the truth.

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VITA

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In the fall of 1945, the author entered the Graduate School at the University of Illinois and in 1946 received the degree of Master of Science in Chemistry. While at Illinois he held a teaching assistantship in the Division of Analytical Chemistry.

He is a member of the following organizations: The American Chemical Society, Sigma Xi and Phi Lambda Upsilon.